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Evguenia Malchukova, Bruno Boizot

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Eugenia Malchukova[(a)] and Bruno Boizot
Laboratoire des Solides Irradiés, UMR 7642 CEA-CNRS-Ecole Polytechnique, 91128 Palaiseau, France

The reduction processes of Eu^{3+} ions were studied using high-temperature melting in air and β-irradiation in aluminoborosilicate glasses by time resolved luminescence and Electron Paramagnetic Resonance spectroscopies. The Eu^{2+} ions produced during the synthesis are characterized by the UV excited broad band luminescence in blue region due to the $4f^65d^1$ to $4f^7$ transition. This Eu^{2+} emission band is the sum of a one short-lived Eu^{2+} sites with weak crystalline field (EuI) and two long-lived sites with strong crystalline field (EuII and EuIII) components. In irradiated glasses, the red-shift of the Eu^{2+} emission band is observed analyzed by an increase of the higher crystalline field Eu^{2+} sites (EuIII) component. The Existence of more than one Eu^{2+} sites with different crystalline field and covalency of surrounding ligands is also discussed in dependence on whether chemically or radiation-induced the Eu^{2+} ions are formed.

It is well-known that the optical properties of materials depend mainly on the nature of the impurities and doping ions inside. Thus, optical activity has been exploited in the investigations of the different matrices by doping them with optically active species such as rare-earth and transition metal ions. Eu^{2+} has electronic transitions between the $4f^7$ ($^8S_{7/2}$) ground state and the $4f^65d^1$ first excited state. These transitions are very sensitive to the surroundings in which the ion is embedded. Due to this characteristic, divalent europium has been employed as a sensitive optical probe.

Oxide glasses are used often as host materials for Rare-Earth (RE) elements because of their high transparency, large range of possible RE environments, and easy way of synthesis. Usually when the glass is melted in air, the rare-earth ions are incorporated in the trivalent oxidation state. The reducing atmosphere, such as H_2 or CO, is generally needed to reduce Eu^{3+} to Eu^{2+} during the synthesis of Eu^{2+} doped luminescent materials. The sol-gel technique is the alternative way to reduce Eu^{3+} ions: this process is appropriate for embedding reduced ions in glasses under moderate conditions of temperature and atmosphere[1,2]. Recently, some research works on reduction of Eu^{3+} into Eu^{2+} in air has been reported in Eu doped Al_2O_3–SiO_2 glasses[3], MO–B_2O_3 glasses (M = Ba, Sr, and Ca)[4] and aluminoborosilicate (ABS) glasses[5]. Indeed, the preparation of Eu^{2+} doped materials in air is more convenient than in reducing atmosphere.

This letter reports Eu^{2+} emission studies in aluminoborosilicate glasses before and after β-irradiation. The purpose is to demonstrate the details of the Eu^{3+} reduction processes in as-prepared and irradiated glasses as well as the peculiarities of Eu^{2+} local environment in both cases.

$64.04SiO_2$-$16.87B_2O_3$-$4.11Al_2O_3$-$12.98Na_2O$-$1.82ZrO_2$ (mol%) aluminoborosilicate (ABS) glass containing nominally 3 wt% (0.55 mol%) of Eu_2O_3 oxide was prepared by high-temperature melting in air. The starting materials SiO_2, H_3BO_3, Al_2O_3, Na_2CO_3, ZrO_2 and Eu_2O_3 were mixed in good proportions and were first heated at 750°C in a Pt crucible during 10 hours. Then, the mixture was melted at 1500°C for one hour and quenched in air on the copper plate. After the synthesis, an annealing at 500 °C during 1-2 hours was effected in order to release mechanical strains. Glass samples in form of tablet (diameter 3-4 cm) were cut into slices of 0.5 mm thickness and polish with the SiC abrasive paper. 2.5 MeV β-irradiations were performed using a Van de Graaff accelerator (Laboratoire des Solides Irradiés, Ecole Polytechnique, France). The current of the electron beam was fixed to 10μA and different integrated doses from 10^6 to 2×10^9 Gy were integrated in each glass samples.

In the obtained ABS glasses the europium ions are found to be in both "+3" and "+2" valence state. Figure 1 shows the emission spectra of pristine and β irradiated (10^9 Gy) ABS glasses containing 3 wt% of Eu_2O_3. In the spectra of both glasses, one can see a series of sharp emission peaks at around 600 nm assigned to the $^5D_0\rightarrow{}^7F_j$ (j=0,1,2…) transitions of the Eu^{3+} ion and a broad band in blue region attributed to the $4f^65d^1\rightarrow{}^8S_{7/2}$ transition of the Eu^{2+} ion. Production of divalent europium ions in both glasses is confirmed by the occurrence of the characteristic EPR signals at g = 4.6 and 6.0 shown in the Figure 2[6,7]. These EPR lines are attributed to Eu^{2+} ions located in strong and weak crystalline field sites, respectively[8,9]. Thus it can be concluded that both high-temperature melting in air and β-irradiation affects the europium valence state. Comparing the emission spectra of these two kind of Eu^{2+} ions production, one can see the significant red shift of the $4f^65d^1\rightarrow{}^8S_{7/2}$ band for the irradiated ABS glass. This difference in the Eu^{2+} emission bands can be explained by the different local environment around radiation-induced Eu^{2+} ions in comparison with chemically formed ones. Indeed, Eu^{2+} ions can be formed from Eu^{3+} ions during the glass synthesis in air in the raw material by chemical reaction through carbon in the glass:

$$Na_2CO_3 \rightarrow Na_2O + CO_2,\ CO_2 \rightarrow C\uparrow + O_2\uparrow,$$
$$C + Eu_2O_3 \rightarrow EuO + CO\uparrow$$
or
$$Na_2CO_3 + Eu_2O_3 \rightarrow Na_2O + 2EuO + CO_2\uparrow.$$

As a result of the reaction, oxygen is removed from the europium surrounding and the local environment of the reduced Eu^{2+} ions is not the same as for inittialy embedded Eu^{3+} ions in terms of the number of oxygens.

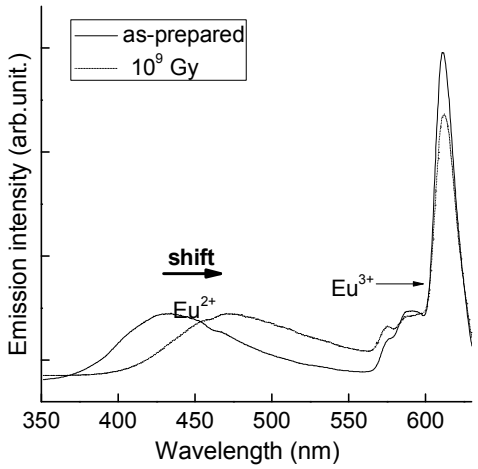

Fig.1. Emission spectra, measured at room temperature, of as-prepared and irradiated ABS glasses containing 3wt% of Eu_2O_3. Excitation with forth harmonic of Nd:YAG laser (266nm)

By contrast in the case of X-irradiated fluoride phosphate and phosphate glasses Ebendor-Heidepriem et al[10]. have been concluded that the absence of structural relaxation around radiation-induced Eu^{2+} ions resuts in the same (or even more) number of surrounding oxygens for both Eu^{2+} and Eu^{3+} ions. Thus the local environment for Eu2+ ions formed chamicallty and by irradiation supposed to be different. However, by our previous investigations it has been shown in non-doped ABS glass that significant structural modifications are occurring under irradiation at 10^9 Gy like densification, polymerization increase, sodium migration and formation of molecular oxygen, as well as defect creation[11-13]. Moreover, rare earth glass doping results in decreases of both the Na^+ and O^{2-} migration and the amount of radiation defects under irradiation[14-15]. We consider therefore that the radiation-induced reduction of Eu^{3+} ions can be accompanied by structural relaxation. Nevertheless, the average surrounding of the radiation-induced Eu^{2+} ions can be different from the chemically-formed one in terms of Eu^{2+} site proportions with different covalency, bond length and strength like suggested in the figure 2 by the modification of the ratio between the g = 6.0 and 4.6 EPR lines.

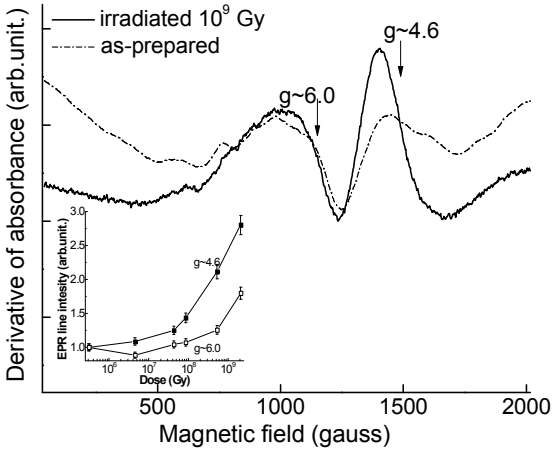

Fig.2. EPR spectra, measured at room temperature, of pristine and irradiated ABS glasses containing 3wt% of Eu_2O_3. in inset – evolution of the sites with g~4.6 and 6.0 as a function of irradiation dose

It is known that depending on the distance, location and the covalence of the surrounding ions, the position (in energy) of $4f^65d^1$ band can vary. In order to examine the influence of β-irradiation on the bonding nature of the Eu^{2+} ions, we measured the emission spectra presented in Figure 3 with different temporal conditions For the ABS glass, a broad emission band assigning to short-lived Eu^{2+} centers (Eu_{Sh-L}) (Gate delay 200 ns, width 500 ns) exhibits several components – a main peak at 435 nm, a shoulder at 456 nm and a weak peak on the low-energy side at ~470 nm and may be attributed to three different kind of Eu^{2+} sites in the ABS glass structure named EuI, EuII and EuIII, respectively (Fig.3a). The significant contribution of the EuI site in the emission and its lowest position (in energy) in comparison with other sites let us consider EuI site as short-lived with weak ligand field around Eu^{2+} ions. As the distance between Eu^{2+} and oxygen ions is shorter, the splitting of the 5d levels is larger at the EuIII site than at the EuII or EuI sites. Consequently, the EuIII site yields a longer wavelength and is characterized by strong crystalline field around Eu^{2+} ions in comparison with EuII or EuI sites. The full-width at half-maximum (FWHM) of the emission band is about 75 nm. As a consequence of irradiation the emission band is shifted as a whole to lower energies and broadened (FWHM is 93 nm). Since the positions of the different components of the Eu^{2+} band are not changed, the red-shift can be attributed to a change under irradiation of the emission intensity ratio between different Eu^{2+} sites. EuI site proportion seems to decreased and the long-wavelength emission assigned to EuII and EuIII sites to be much intense for irradiated glass. These evolutions of the emission spectra in irradiated samples could be correlated to both energy transfer between weak and strong crystalline fields sites or to an increase of the Eu^{2+} ions at sites with strong crystal field. In addition, the broadening of the whole $4f^65d^1$ emission band as a whole reveals only relative contribution of all sites.

The changing of the temporal conditions for the emission detection modifies the Eu^{2+} ions emission spectrum (Fig.3b). If we use a delay time of 3 μs and a gate width of 10μs, the short-lived EuI site is quenched and the resulting spectrum represents only the contribution of two more long-lived EuII and EuIII sites (Eu_{L-L}). The shift of $4f^65d^1$ band of Eu^{2+} ion as a whole to lower energies in comparison with emission spectrum measured with low delay (Fig.3a) confirms the presence of more covalent surrounding around EuII and EuIII sites. According to this result, long-lived EuII and EuIII sites are really characterized by strong crystalline field around Eu^{2+} ion. The differences in the emission spectrum of Eu^{2+} ions in irradiated glass (Fig.3b) are difficult to estimate because of the strong overlap with broad line assigned to the intrinsic defects of ABS matrix which is detected in this region (maximum at 514 nm).

We suppose however that the difference in the emission properties of as-prepared and irradiated ABS

glasses is strongly related to the crystal-field environment (e.g., covalency, bond length and crystal-field strength). The results obtained by means of emission measurement are confirmed by EPR data (Fig.2). Indeed, in both as-prepared and irradiated ABS glass, Eu^{2+} ions are located in two different sites with weak (g~6.0) and strong (g~4.6) crystalline field

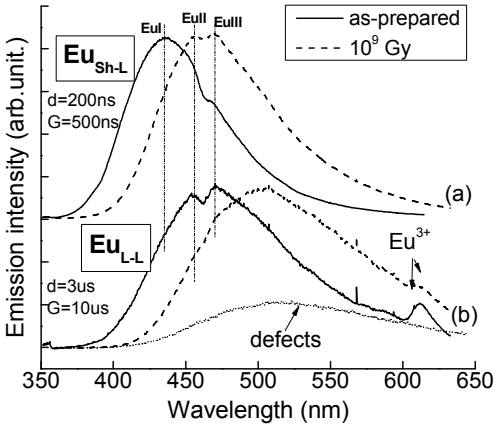

Fig.3. Emission spectra, measured at room temperature, of pristine and irradiated ABS glasses containing 3wt% of Eu_2O_3, measured at different conditions for emission registration (355 nm).

Exposure to β-irradiation leads to the increase of the relative proportion of Eu^{2+} sites with high crystal-field. According to emission spectra results, the ligand field at the EuI site is weaker than at the EuIII site and we also observed under irradiation an emission intensity increases related to the increase of the Eu^{2+} ions at the EuIII sites. In addition, EuIII site was found in as-prepared ABS glass as long-lived Eu^{2+} centers. Hence, the emission band at 435 nm can be ascribed to the EuI short-lived site and the other one at 470 nm to the EuIII long-lived more covalent site.

In conclusion, by the combination of two spectroscopic techniques (EPR and luminescence), it has been shown the presence of at least two Eu^{2+} sites in ABS glasses characterized by different crystal field strength and covalency. The relative proportion between sites depends strongly on the processes for Eu^{2+} ions production in ABS glass during the high-temperature melting in air and β-irradiation.

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